0.1 Schrödinger Equation in 2-dimensional system

In HW problem set 5 , we introduced a simpleminded system describing the ammonia (NH_3) molecule, consisting of a plane spanned by the 3 hydrogen atoms and a single N atom being either above or below the plane. Our simple HS has only 2 dimensions, corresponding to the two possible states of the N atom relative to the plane of 3 N atoms (above or below). This yields to basis vectors $|1\rangle, |2\rangle$ which are eigenvectors to the observable measuring the z-position of the N atom relative to the hydrogen plane, Z:

$$\begin{aligned} Z|1\rangle &= +z_0|1\rangle \\ Z|2\rangle &= -z_0|2\rangle \end{aligned} \tag{1}$$

We can thus represent any state in the HS as

$$|\Psi\rangle = a|1\rangle + b|2\rangle = \begin{pmatrix} a \\ b \end{pmatrix}$$

The Hamiltonian from HW problem set 5 in matrix form is given by

$$H_{i,j} = \begin{pmatrix} E & \text{-V} \\ -V & \text{E} \end{pmatrix}$$

Applying this to the Schr̈odinger Equation:

$$i\hbar \begin{pmatrix} \dot{a} \\ \dot{b} \end{pmatrix} = \begin{pmatrix} E & \text{-V} \\ -V & \text{E} \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} Ea - Vb \\ -Va + Eb \end{pmatrix}$$

Adding up the two equations

$$i\hbar(\dot{a} + \dot{b}) = (Ea + Eb - Va - Vb) = (E - V)(a + b)$$

$$\dot{c} = (\dot{a} + \dot{b})$$

$$i\hbar\dot{c} = (E - V)c; \quad \dot{c} = \frac{(E - V)c}{i\hbar}$$

$$c(t) = c_0 e^{\frac{(E-V)t}{i\hbar}}; \quad (a + b)(t) = (a + b)(t_0)e^{\frac{(E-V)t}{i\hbar}}$$

Subtracting the two

$$i\hbar(\dot{a} - \dot{b}) = (Ea - Vb + Va - Eb) = (E + V)(a - b)$$

$$(a-b)(t) = (a-b)(t_0)e^{\frac{(E+V)t}{i\hbar}}$$

$$a(t) = \frac{1}{2}\left[(a+b)(t_0)e^{\frac{(E-V)t}{i\hbar}} + (a-b)(t_0)e^{\frac{(E+V)t}{i\hbar}}\right]$$
$$b(t) = \frac{1}{2}\left[(a+b)(t_0)e^{\frac{(E-V)t}{i\hbar}} - (a-b)(t_0)e^{\frac{(E+V)t}{i\hbar}}\right]$$

$$a(t) = e^{\frac{Et}{i\hbar}}\frac{1}{2}\left[a_0\left(e^{\frac{-Vt}{i\hbar}} + e^{\frac{Vt}{i\hbar}}\right) + b_0\left(e^{\frac{-Vt}{i\hbar}} - e^{\frac{Vt}{i\hbar}}\right)\right]$$

$$a(t) = e^{\frac{-iEt}{\hbar}}\left[a_0\cos\frac{Vt}{\hbar} + ib_0\sin\frac{Vt}{\hbar}\right]$$
$$b(t) = e^{\frac{-iEt}{\hbar}}\left[b_0\cos\frac{Vt}{\hbar} + ia_0\sin\frac{Vt}{\hbar}\right]$$

Over all time

$$|\Psi\rangle(t) = e^{\frac{-iEt}{\hbar}}\begin{pmatrix} a_0\cos\frac{Vt}{\hbar} + ib_0\sin\frac{Vt}{\hbar} \\ b_0\cos\frac{Vt}{\hbar} + ia_0\sin\frac{Vt}{\hbar}\end{pmatrix} = e^{\frac{-iEt}{\hbar}}\begin{pmatrix}\cos\frac{Vt}{\hbar} & i\sin\frac{Vt}{\hbar} \\ i\sin\frac{Vt}{\hbar} & \cos\frac{Vt}{\hbar}\end{pmatrix}|\Psi\rangle(0)$$

Given initial conditions, you can determine the state of the system at any time. Assume, e.g., that at

$$t = 0, \quad |\Psi\rangle(0) = \begin{pmatrix}1\\0\end{pmatrix}, a_0 = 1, b_0 = 0 \quad \text{the atom is on top}$$

then we find at

$$t = T = \frac{\pi\hbar}{2V}, \quad |\Psi\rangle(T) = e^{\frac{-iET}{\hbar}}\begin{pmatrix}0\\i\end{pmatrix} \quad \text{the system will have flipped with}$$

the nitrogen atom at the bottom.

The system moves up and down periodically. By making a measurement of Z we get either one of the eigenvalues of this observable with probability $\langle 1,2|\,\psi(t)\rangle$. At $t = 0$ there is a 100% chance of getting $\begin{pmatrix}1\\0\end{pmatrix}$. Even though the system is perfect, after $t = 0$, it changes to a superposition of the two eigenvectors. The outcome still has to be either $\begin{pmatrix}1\\0\end{pmatrix}$ or $\begin{pmatrix}0\\-1\end{pmatrix}$, but the probability of each state has to be calculated.

$$Prob(+1) = \left| \left\langle \begin{pmatrix} 1 \\ 0 \end{pmatrix} \right| |\Psi(t)\rangle \right|^2$$

$$= \left| e^{\frac{-iEt}{\hbar}} \cos \frac{Vt}{\hbar} \right|^2$$

$$= \cos^2 \frac{Vt}{\hbar}$$

$$Prob(-1) = \sin^2 \frac{Vt}{\hbar}$$

The sum of the 2 probabilities always gives 1. If the probability of either is 100%, then that is the state of the system.

We can use the Hamiltonian matrix, $H = \begin{pmatrix} E & \text{-V} \\ -V & \text{E} \end{pmatrix}$ by replacing it in the formal solution $|\Psi\rangle(t) = e^{\frac{iHt}{\hbar}} |\Psi\rangle(0)$

$$e^{\frac{it}{\hbar}\begin{pmatrix} E & \text{-V} \\ -V & \text{E} \end{pmatrix}} = 1 + \frac{it}{\hbar} \begin{pmatrix} E & \text{-V} \\ -V & \text{E} \end{pmatrix} \cdots$$

Using $e^{(a+b)} = e^a e^b$

$$= e^{\frac{-it}{\hbar}\begin{pmatrix} E & 0 \\ 0 & \text{E} \end{pmatrix}} e^{\frac{it}{\hbar}\begin{pmatrix} 0 & \text{-V} \\ -V & 0 \end{pmatrix}}$$

$$= e^{\frac{-iEt}{\hbar}} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \left[1 + \begin{pmatrix} 0 & iVt\hbar^{-1} \\ iVt\hbar^{-1} & 0 \end{pmatrix} + \frac{1}{2} \begin{pmatrix} iV^2t^2\hbar^{-2} & 0 \\ 0 & iV^2t^2\hbar^{-2} \end{pmatrix} \cdots \right]$$

yields the propagator $\quad U(t) = e^{\frac{-iEt}{\hbar}} \begin{pmatrix} \cos\frac{Vt}{\hbar} & i\sin\frac{Vt}{\hbar} \\ i\sin\frac{Vt}{\hbar} & \cos\frac{Vt}{\hbar} \end{pmatrix}$

This is of course the same matrix we found earlier, confirming the equivalence of these two approaches.

If H is Hermitian, then U is Unitary and tells what the state of the system is at any time t

$$|\Psi\rangle(t) = U(t)\,|\Psi\rangle(0)$$

$$|\Psi\rangle(0) = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

One more way of looking at the Schrodinger equation is to look first for the eigenvalues

$$H\left|\phi_n\right\rangle = E_n\left|\phi_n\right\rangle$$

Any state

$$\left|\psi\right\rangle(t) = \sum_n \left|\phi_n\right\rangle\left\langle\phi_n\right|\left.\Psi\right\rangle(t)$$

$$i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = H\sum_n \left|\phi_n\right\rangle\left\langle\phi_n\right|\left.\Psi\right\rangle$$

$$i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = \sum_n E_n\left|\phi_n\right\rangle\left\langle\phi_n\right|\left.\Psi\right\rangle$$

If Ψ is an eigenfunction, $\left|\Psi\right\rangle = \left|\phi_n\right\rangle$

$$i\hbar\frac{\partial}{\partial t}\left|\Psi\right\rangle = E_n\left|\phi_n\right\rangle$$

E_n becomes a number so we can write

$$\left|\Psi\right\rangle(t) = e^{\frac{iE_nt}{\hbar}}\left|\Psi\right\rangle(0)$$

This means that the initial state vector at $t = 0$ simply gets multiplied with a complex phase at all t and doesn't change the underlying physical state (stationary = time-independent solutions to the Schrödinger equation). The states can be considered stationary since they don't change over time. They also tend to be stable since the expectation value of any observable is constant:

$$\langle\mathcal{O}\rangle(t) = \left\langle\phi_n(0)\right|e^{\frac{iE_nt}{\hbar}}\mathcal{O}e^{\frac{-iE_nt}{\hbar}}\left|\phi_n(0)\right\rangle = \langle\mathcal{O}\rangle(0)$$

This means that, for instance, a stationary state cannot radiate electromagnetic waves (which requires an oscillating dipole moment, i.e. a time-dependent expectation value for X).

As shown above, any wavefunction $\Psi(t = 0)$ can be broken down as a linear superposition of the eigenstates $\left|\phi_n\right\rangle$ of H:

$$\left|\psi(0)\right\rangle = \sum a_n(0)\left|\phi_n\right\rangle$$

with

$$\left\langle\phi_n\right|\left.\psi(0)\right\rangle = a_n(0)$$

$$a_n(t) = e^{\frac{-iE_n t}{\hbar}} a_n(0)$$

The coefficients follow the rule

$$|\Psi\rangle\,(t) = \sum a_n(0) e^{\frac{-iE_n t}{\hbar}}\,|\phi_n\rangle$$

Now for any state we have

$$|\Psi(t)\rangle = \sum_n \langle\phi_n(0)|\;\Psi(0)\rangle\, e^{\frac{-iE_n t}{\hbar}}\,|\phi_n(0)\rangle$$

(ϕ_n is always taken at $t = 0$.)

It is easy to show that this gives once again the same result when using the eigenstates and eigenvalues for H found in HW problem set 5.

0.2 Uncertainty Principle

Recall that when you measure an observable Ω you get ω_i, some eigenvalue of the observable. When you predict a measurement of Ω, you must predict a range of probabilities associated with each eigenstate of that observable.

Expectation Value

$$\langle\Omega\rangle = \sum_i \omega_i P(\omega_i) = \langle\Psi \mid \Omega \mid \Psi\rangle$$

RMS a.k.a. Standard Deviation a.k.a. σ

$$\langle(\Omega - \langle\Omega\rangle)^2\rangle = \sum_i (\omega_i - \langle\Omega\rangle)^2\, P(\omega_i) = (\Delta\Omega)^2$$

Suppose we have another operator defined by

$$\hat{\Omega} = \Omega - \langle\Omega\rangle_\Psi \mathbb{1}$$

Then

$$(\Delta\Omega)^2 = \langle\Psi \mid \hat{\Omega}^2 \mid \Psi\rangle = \langle\hat{\Omega}\Psi \mid \hat{\Omega}\Psi\rangle = \Big|\mid \hat{\Omega}\Psi\rangle\Big|^2$$

Let's conjure up another operator Λ, then

$$(\Delta\Lambda)^2 = \Big|\mid \hat{\Lambda}\Psi\rangle\Big|^2$$

We can derive a relationship between any two operators by using the following relation as well as the Schwartz inequality

$$\hat{\Omega}\hat{\Lambda} = \frac{\hat{\Omega}\hat{\Lambda} + \hat{\Lambda}\hat{\Omega}}{2} + \frac{\hat{\Omega}\hat{\Lambda} - \hat{\Lambda}\hat{\Omega}}{2} = \frac{1}{2}\left[\hat{\Omega}, \hat{\Lambda}\right]_+ + \frac{1}{2}\left[\hat{\Omega}, \hat{\Lambda}\right]$$

Then,

$$\begin{aligned}
&(\Delta\Omega)^2(\Delta\Lambda)^2 = ? \\
&(\Delta\Omega)^2(\Delta\Lambda)^2 \geq \left|\langle\Psi \mid \hat{\Omega}\hat{\Lambda} \mid \Psi\rangle\right|^2 \\
&(\Delta\Omega)^2(\Delta\Lambda)^2 \geq \left|\frac{1}{2}\langle\Psi \mid [\hat{\Omega}, \hat{\Lambda}]_+ \mid \Psi\rangle + \frac{1}{2}\langle\Psi \mid [\hat{\Omega}, \hat{\Lambda}] \mid \Psi\rangle\right|^2 \\
&(\Delta\Omega)^2(\Delta\Lambda)^2 \geq \frac{1}{4}\left|\langle\Psi \mid [\Omega, \Lambda] \mid \Psi\rangle\right|^2
\end{aligned}$$

(The last equation follows because the first scalar product in the previous equation must be real - assuming both operators are Hermitian, you showed their anti-commutator is Hermitian - while the second term must be purely imaginary, again as shown before. This in turn means that the absolute square of the whole impression is the sum of the squares of the two individual terms, which is of course larger than just one of these terms squared).

Thus we obtain a generalized uncertainty principle

$$\Delta\Omega\Delta\Lambda \geq \frac{1}{2}\left|\langle\Psi \mid [\Omega, \Lambda] \mid \Psi\rangle\right|$$

As an example, recall that $[x, p] = i\hbar\mathbb{1}$, $p = \frac{\hbar}{i}\frac{\partial}{\partial x}$ then...

$$\Delta p\Delta x \geq \frac{\hbar}{2}$$

It is important to understand that the actual result for the product $\Delta\Omega_\psi\Delta\Lambda_\psi$ depends not only the operators themselves (and, in particular, their commutator), but also on the state $|\psi\rangle$. In particular, if $|\psi\rangle$ is an eigenvector to either one of the two operators, the product of uncertainties will vanish. On the other hand, it is also important to realize that, very often, the actual product of uncertainties can be (much) larger than predicted by the r.h.s., since we dropped the anticommutator term and it is only an inequality. Finally, make sure you understand that the two uncertainties $\Delta\Omega_\psi$ and $\Delta\Lambda_\psi$

are the *intrinsic* uncertainties encoded in the wave functions; they do **not** tell us what the outcome is if we measure first Ω and then Λ or vice versa, but only what the uncertainty of the *predicted* outcome is if we decide to measure *either* of them.